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**Nickel Carbonyl Ambient Monitor**

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Prepared For

The Ontario Ministry of the Environment  
Toronto, Ontario

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Nickel Carbonyl Ambient Monitor

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Final Report

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Le but de ce travail contractuel consistait à produire un instrument capable de mesurer les concentrations de nickel carbonyle dans l'air ambiant jusqu'à la norme provinciale de 0,5  $\mu\text{g}/\text{m}^{-3}$  (70 PPT) en vigueur en Ontario.

La technique analytique choisie fait appel à la chimiluminescence qui s'opère lorsqu'il y a réaction entre le nickel carbonyle et l'ozone.

Nous avons mis au point un instrument capable de mesurer, jusqu'aux normes provinciales les plus basses, les concentrations de nickel carbonyle dans l'air. Cet instrument s'est avéré capable de détecter une limite de 10 PPT.

Nous avons également mis au point un plan pour le calibrage *in situ* à partir d'un cylindre contenant du nickel carbonyle, ainsi qu'une technique pour le calibrage des cylindres.

## Nickel Carbonyl Ambient Monitor

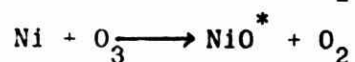
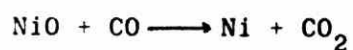
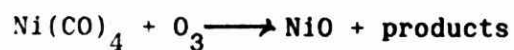
### Introduction

The purpose of the contract was to produce an instrument capable of measuring ambient levels of Nickel Carbonyl down to the Ontario Provincial standard of  $0.5 \mu\text{gm}^{-3}$  (70 ppt).

The analytical technique that was chosen uses the chemiluminescence which results when Nickel Carbonyl is reacted with ozone.

### General Theory of Operation

The gas-phase reaction of Nickel Carbonyl ( $\text{Ni}(\text{CO})_4$ ) and ozone ( $\text{O}_3$ ) in the presence of carbon monoxide (CO) produces a characteristic luminescence with an intensity linearly proportional to the concentration of Nickel Carbonyl. Specifically,



Light emission results when electronically excited NiO molecules decay to lower energy states.

The ambient air sample enters the instrument through a single flow control capillary. The sample is then mixed with carbon monoxide and ozone and admitted to the reaction chamber where the chemiluminescence is measured. An output signal is continuously generated which records the level measured.



### Instrument Modification

The Thermoelectron Corporation (TECO) markets a Nickel Carbonyl monitor, model 14N, but the specifications indicate it is not sufficiently sensitive for Ministry requirements. The detection limit is listed as  $0.7 \mu\text{gm}^{-3}$  (.1ppb) Thus for this contract this instrument would have needed to be modified. The Nickel Carbonyl instrument is a modified model 14B/E NO/NO<sub>x</sub> instrument. Since modifications would have been required to the Nickel Carbonyl instrument, it was decided it would be more cost effective to purchase the NO/NO<sub>x</sub> instrument and modify it to measure Nickel Carbonyl at the required sensitivity.

The following modifications were made to the commercial NO/NO<sub>x</sub> instrument:

a) The volume of the reaction vessel was increased from 10 to 100 cubic centimeters. This increases the number of Nickel atoms being viewed by the photomultiplier and thus increases the sensitivity.

b) The air flow through the system was increased which increases the number of Nickel atoms passing through the cell and thus the sensitivity.

c) The red filter in front of the photomultiplier was replaced with an Andover 023FG11-50 blue filter. This was selected to maximize transmission of the NiO\* chemiluminescence while rejecting the NO<sub>2</sub>\* chemiluminescence from NO and the FeO\* chemiluminescence from Fe(CO)<sub>5</sub>. In this way the selectivity toward Ni(CO)<sub>4</sub> was assured.

d) An additional plumbing line to allow addition of CO was included. It was found necessary to include a needle valve on this line to optimize instrument sensitivity. A scrubber containing iodine and activated charcoal was included on this line to remove any carbonyl in the carbon monoxide

cylinder. (In the course of this work it was found that normal CP grade carbon monoxide contains extremely variable amounts of carbonyls. We recommend a high purity grade of CO in an aluminum cylinder be used for this instrument.)

e) The sample and hold electronics of 14 B/E is now redundant and has been bypassed. The signal from the photomultiplier now passes through an amplifier, a temperature compensation board, and switch is then filtered and appears as the recorder output. None of the original control electronics is used.

f) While running instrument tests the photomultiplier tube envelope fractured. Thus we had to replace this tube. A direct replacement was quoted as being \$3,000. The high cost is related to the low quantum efficiency of photomultipliers in the red end of the spectrum. However, for this instrument we block the red end of the spectrum. As a result a cheaper photomultiplier could be used. We purchased a Hamamatsu Model R329 tube for \$300 U.S. which could be used without modifying the instrument. In addition this tube has a far lower dark current at room temperature and while it was higher than the cooled tube the improvement was so small we decided to disconnect the thermoelectric cooler.

g) The final modification to the instrument was to replace the supplied pump with a rotary vacuum pump. It by found that using the diaphragm pump that the relationship between signal and Nickel Carbonyl concentration was not linear. It was found that by lowering the cell pressure linearity was achieved. This necessitated the replacement of the diaphragm pump with a rotary vacuum pump. It should be noted here that ozone reacts with rotary pump oil in making it very thick and potentially capable of seizing the pump.

Two precautions need to be taken to lengthen the life of the pump. Firstly the TECO ozone destruction catalyst should be placed between the instrument and the pump, not after the pump as with the 14B/E. Secondly the pump oil should be replaced regularly.

### Instrument Tests

Before delivering the instrument many tests were performed to ensure it met the contract standards. The two instrument parameters that were of most concern were sensitivity (and its associated parameter, detection limit) and linearity. We also examined some parameters related to the reliability of the instrument. The bulk of the tests however related to the development of a calibration and sampling protocol.

### Instrument Linearity

This section of the work was expected to be relatively straightforward. The mechanism for this reaction is well known and predicts a linear relationship between signal and Nickel Carbonyl concentration. Varying parameters such as air flow, ozone flow and reaction cell pressure would be expected to change the sensitivity (the signal per unit of concentration) but a linear relationship would be expected for any parameter combination. (This is not strictly true for low ozone concentrations but this case is never encountered so was not considered)

Figure I shows the linearity check run for an early geometry and using the TECO supplied pump. Non linearity is clear. For a halving of the Nickel Carbonyl concentration the signal drops by a factor of just over 2 whereas halving the concentration again drops the signal by an order of magnitude.

We found both the signal magnitude to increase and the signal concentration relation to more closely approach linearity as the air ozone and the carbon monoxide were premixed closer to the reaction vessel. The prereactor in particular showed some irreproducible behaviour and since it appeared not to be necessary for NO signal rejection it was removed. We noted some improvement when the air was dried by a Nafion 811X tubing drier

prior to analysis. This drier is recommended for all uses of this instrument. We tried many combinations of flows and plumbing schemes but it was not until we lowered the reaction vessel pressure that linear behaviour became reproducible. Figure II shows the same plot as Figure I but for the final system geometry and shows the instrument has a linear relationship between signal and Nickel Carbonyl concentration.

Note:

It is important to understand how the linearity tests were performed. A constant ambient air flow was doped with varying flows from the Nickel Carbonyl cylinder. We used Hastings mass flowmeter for the flow measurements but found that the heat of the flowmeter was sufficient to decompose the  $\text{Ni(CO)}_4$ . Thus the protocol was to set the Nickel Carbonyl flow and measure it using the flowmeter. The signal on the instrument was zero at this time. We then turned the flowmeter off and as it cooled the signal rose. After 15 minutes the signal stabilized and this value was used. The flowmeter was turned on again to ensure the flow had not changed. This procedure was followed for all flows, i.e. for all concentrations.

Sensitivity and Detection Limit

Once linearity was assured it was then possible to determine the sensitivity and detection limit. Using the scale remaining from the  $\text{NO/NO}_x$  application we found the sensitivity to be 4 concentration units for 1 ppb of Nickel Carbonyl. This gives a sensitivity of 4 concentration units per ppb. The peak to peak noise on the background is 0.02 concentration units corresponding to <10 ppt of Nickel Carbonyl. Thus using the instrument with a chart recorder output the detection limit is 10 ppt and could be improved using signal averaging.

### Sensitivity

A concern was that the instrument may still respond to NO. We initially took two approaches to removing the NO interference. Firstly we replaced the red filter in front of the photomultiplier with a blue filter which cuts off the NO<sub>2</sub> emission. In addition we installed a prereactor in the sample line. The object here was to mix ozone with the air upstream of the prereactor. The residence time of air in the prereactor was such that all chemiluminescence due to NO had decayed before the sample reached the cell and was detected. Since the nickel carbonyl detection relies on a catalytic cycle it would be unaffected by the prereactor. We found that changing the filter alone was sufficient to discriminate against NO. The prereactor was found to contribute to the non linearity problem and was removed.

The instrument was supplied a sample of 50 ppb NO to which it did not respond.

### Calibration Sources

#### a) Permeation Source.

The initial attempt at an in situ calibration source was a permeation device. In this case Nickel Carbonyl in a container at 35°C was separated from the air stream going to the instrument by a wafer of teflon. The concentration gradient across the wafer then drives diffusion, or permeation, of Nickel Carbonyl through the wafer. A constant mass of Nickel Carbonyl would pass through the wafer which could be fed to the instrument for calibration. We used wafer as low as .010" thick but were unable to get sufficiently high permeation rates for a sensible calibration source.

### Diffusion Source

The diffusion source is similar in principle to the permeation source except that the wafer is replaced by a short length of capillary tubing. This worked much better than the permeation source but was found to be more variable than could be tolerated. On opening the source we found nickel deposits on many occasions showing Nickel Carbonyl decomposition in the capillary which changes the geometry and thus the diffusion rate. The diffusion device also showed variable rates when the unit was moved showing the effects, we believe, of Nickel Carbonyl being splashed within the device.

### Calibration cylinders

At the beginning of this project we attempted to find a supplier of gas cylinders of Nickel Carbonyl at part per million mixtures. We were successful but believed they were overly expensive and since we expected the permeation device to work we did not pursue the option.

The failure of permeation and diffusion devices left us with only the cylinder as an option. The long lead time and cost of the commercial product led us to make our own cylinders. We had a passivated aluminum cylinder pressure tested and a new valve fitted. In this we made mixtures of Nickel Carbonyl in Nitrogen by pumping the cylinder to  $10^{-5}$  Torr, adding 10's of Torr of  $\text{Ni(CO)}_4$  and filling the cylinder to over 1000 psi with nitrogen. We then calibrated these cylinders regularly. We have seen substantial decay of the standard. We feel this is largely due to decomposition within the cylinder. This could be improved by making the mixture in carbon monoxide rather than nitrogen, a procedure which is done by the commercial supplier but which we were reluctant to do.

We thus recommend the purchase of standard Nickel Carbonyl standards in carbon monoxide but in light of our experience we recommend regular calibrations until confidence in the stability of the standard is established.

#### Calibration of Nickel Carbonyl Tanks

To determine the concentration of Nickel Carbonyl in cylinders an independent absolute analysis system was developed. The principle is to take on some of the gas mixture and collect the Nickel Carbonyl in a solution. The nickel is oxidized to  $\text{Ni}^{\text{II}}$  and complexed with diethyl dithiocarbamate to produce a product with a very strong UV absorption spectrum with a known extinction coefficient. The concentration of the complex is determined by UV absorption allowing the determination of the amount of Nickel Carbonyl in the original sample. By measuring the flow of the gas mixture and the time taken to collect the sample the concentration of Nickel carbonyl can be determined.

#### Procedure

The Nickel Carbonyl tank is connected to a bubbler containing approximately 30 ml of 1:1 nitric acid. The output from the bubbler is connected to a flowmeter to determine the flow (we used a soap bubble meter). The gas mixture was flowed through the bubbler at a rate of about 50 sccm for 30-60 minutes. The nitric acid dissolved the Nickel Carbonyl and oxidized it to  $\text{Ni}^{\text{II}}$ . The sample was washed from the bubbler into a 50 ml volumetric flask for analysis as  $\text{Ni}^{\text{II}}$ .



An aqueous solution of 0.1% sodium diethyldithiocarbamate (BDH AnalaR grade) was prepared with water which was purified by double-distillation over  $\text{KMnO}_4$  followed by passage through a Barnstead organic removal cartridge and two Barnstead mixed resin ultrapure cartridges. This solution was extracted with successive portions of carbon tetrachloride (BDH Assured, ACS grade) until the  $\text{CCl}_4$  layer was colourless.

The pH of the 1:1 nitric acid solution was adjusted to the proper range for complexation with diethyldithiocarbamate by the addition of ammonium hydroxide (ACS grade). The pH was tested with colorpHast Indicator sticks to ensure that it was between 8.5 and 9.0. Once the proper pH was achieved, 2 mL of the sodium diethyldithiocarbamate was added and the solution was transferred to a separatory funnel. Two milliliters of carbon tetrachloride was added to the solution followed by vigorous shaking for at least two minutes. The  $\text{CCl}_4$  layer was then collected in a 10 mL volumetric flask. The extractions were continued until the volumetric flask was filled to the mark. The electronic spectrum of this solution was then recorded over the range 300 to 500 nm using quartz cells and a Hitachi-Perkin Elmer Microprocessor model 340 spectrometer.

### Discussion

The number of moles of nickel present in each sample was determined by the expression

$$\text{moles of Ni} = 2.84 \times 10^{-7} A_{328\text{nm}} \quad (1)$$

based on the extinction coefficient given in Chilton's article [1]. The concentration of  $\text{Ni(CO)}_4$  could then be determined by dividing this value by the product of the flow rate and time of flow.

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[1] J.M. Chilton, Anal. Chem., 25, 1274-1275 (1953).

### Conclusion

An instrument capable of measuring Nickel Carbonyl concentrations in the air down to the Ontario standards has been developed.

It has been shown to have a detection limit of 10 ppt.

A protocol for in-situ calibration from a cylinder containing Nickel Carbonyl has been developed, as has a technique for calibration of cylinders.

### Acknowledgement

We are indebted to the Ontario Ministry of the Environment for support of this work and would like to acknowledge useful discussions with W.C. Tam, A. Szakolcai of the Ministry's Air Resources Branch and R. Potvin of Northeast Region.

V. Antunes and P. Sum ably performed much of the experimental work.

# NICKEL CARBONYL INSTRUMENT

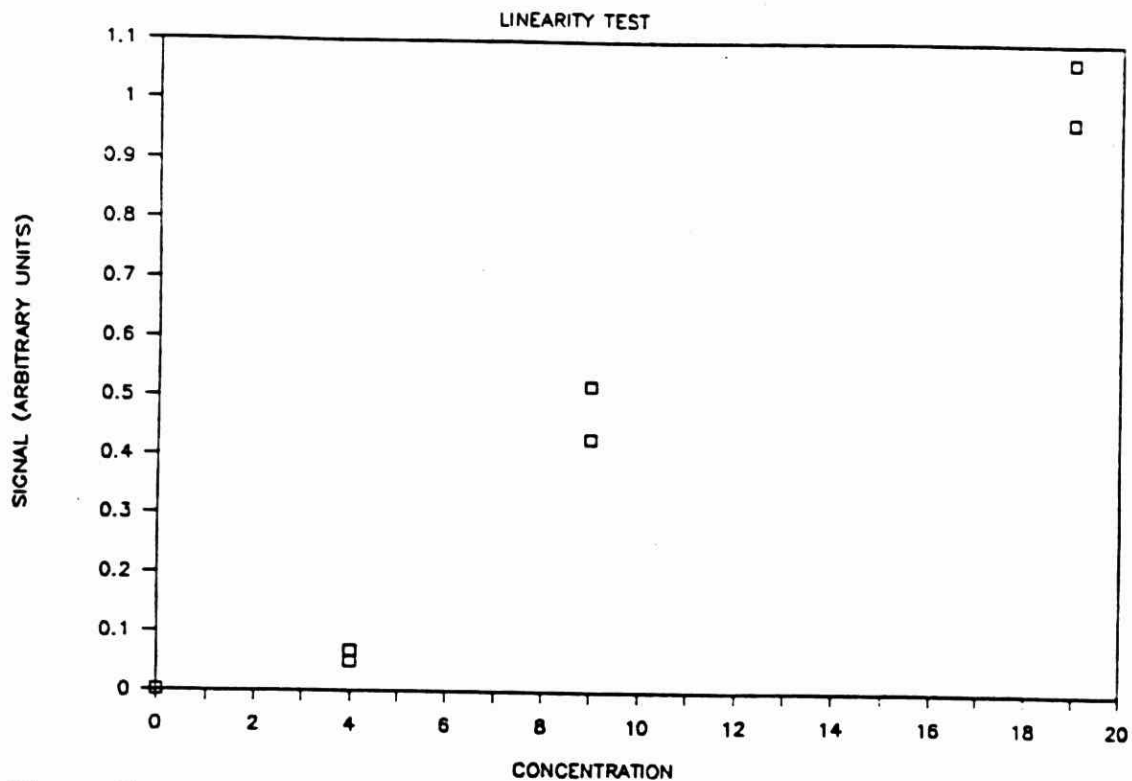


Figure I

Nickel Carbonyl instrument response showing strong non linearity

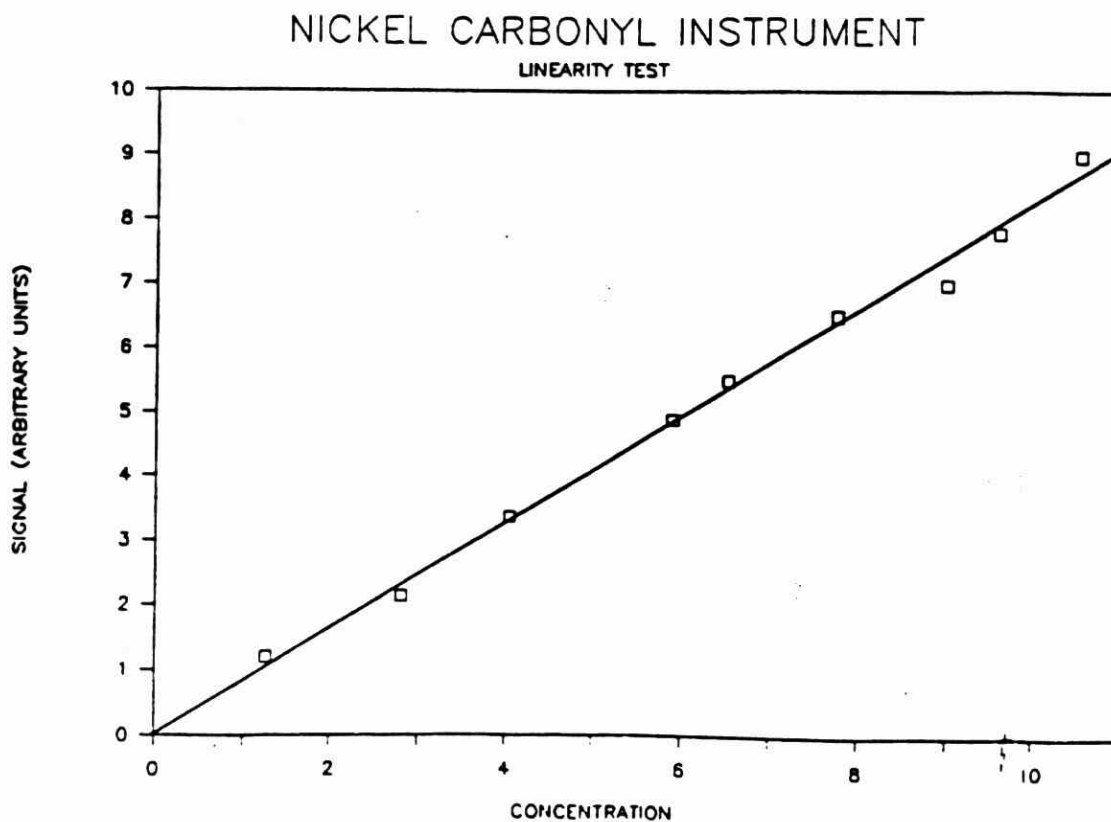


Figure II

Nickel Carbonyl instrument response using final configuration - showing linear response



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